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Accretion product formation from self- and cross-reactions of RO_2 radicals in the atmosphere

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Abstract

Hydrocarbons are emitted into Earth´s atmosphere in very large quantities by human and biogenic activities. Their atmospheric oxidation processes almost exclusively form RO_2 radicals as reactive intermediates whose atmospheric fate is not fully discovered yet. Here we show that gas-phase reactions of two RO_2 radicals produce accretion products composed of the carbon backbone of both reactants. RO_2 radicals bearing functional groups show fast accretion product formation rates competing with those of the corresponding reactions with NO and HO_2. This pathway, not considered yet in the modelling of atmospheric processes, can be important, or even dominant for the fate of RO_2 radicals in all areas of the atmosphere. Moreover, the formed accretion products can be featured by remarkably low vapour pressure characterizing them as effective source for secondary organic aerosol.

The global emission rate of non-methane hydrocarbons from vegetation and human activities into the atmosphere is estimated to be about 1.3×10^9 metric tons of carbon per year.[1] Their gas-phase degradation process is mainly initiated by the reaction with hydroxyl (OH) or nitrate (NO_3) radicals, chlorine atoms or ozone (O_3).[2] After initial attack of the oxidant, RO_2 radicals are almost exclusively formed as intermediates, which rapidly react further with NO, HO_2 or other RO_2 radicals or via RO_2 radical self-reaction. More recently, also effective RO_2 radical isomerization steps have been discovered, i.e. the RO_2 autoxidation[3] and the endo-cyclization of unsaturated RO_2 radicals[4] finally leading to higher functionalization of the RO_2 radicals.

It is currently accepted that the main products of the self- and cross-reaction of RO_2 radicals are either the corresponding oxyl radicals (RO), pathway (1a), or an alcohol (ROH) in conjunction with a carbonyl (R´(-H,=O)), pathway (1b).[5]

$$RO_2 + R´O_2 \rightarrow RO + R´O + O_2 \quad (1a)$$

$$\rightarrow ROH + R´(-H,=O) + O_2 \quad (1b)$$

As a result of earlier studies, the formation of dialkyl peroxides has been discussed additionally, pathway (1c). Stated peroxide yields from the self-reaction of the simplest RO_2 radicals, $RO_2 = R´O_2 = CH_3O_2$, $C_2H_5O_2$ or $CH_3C(O)O_2$, were reported to be small.[6]

$$RO_2 + R´O_2 \rightarrow ROOR´ + O_2 \quad (1c)$$

The relevance of pathway (1c) has not been investigated yet for RO_2 radicals other than for the small model RO_2 radicals and is currently not considered in atmospheric modelling.[7] However, recent experimental findings, especially from gas-phase ozonolysis of cyclohexene[8] and terpenes[3b,3c,9], point to accretion product formation that could be at least partly explained by a process according to pathway (1c). It should be noted that ROOR´ formation is also discussed for RO_2 radical reactions occurring in the liquid phase.[10]

Here we report on an experimental study focusing on the formation of accretion products with the chemical composition ROOR´ that can be explained via pathway (1c). The investigations have been performed in a free-jet flow system under atmospheric conditions in the absence of noticeable wall effects[3d,8b]. RO_2 radicals and accretion products from different reaction systems were probed simultaneously by means of latest mass spectrometric techniques, which were recently described[3d,11] or are applied here for the first time. A detailed description of the experimental approach is given in Supplementary Information.

The findings of this study demonstrate the general validity of accretion product formation via pathway (1c) or related pathways for all possible combinations of RO_2 radicals in a particular reaction system. It is to be noted that, at the present stage, we cannot prove the peroxide structure of ROOR´, we merely show the formation of products with an exact mass that is in accordance with the chemical composition ROOR´.

First, product formation from the OH radical initiated oxidation of 1,3,5-trimethylbenzene has been investigated using ozonolysis of tetramethylethylene (TME) as OH radical source. 1,3,5-trimethylbenzene represents an example of aromatic compounds, which are important emissions in urban areas.[12] Measured concentrations of the main RO_2 radicals, i.e. $CH_3C(O)CH_2O_2$ from TME ozonolysis[13] and $HO\text{-}C_9H_{12}(O_2)_xO_2$ with x = 1 - 3 from the aromatic[14], increased almost linearly with rising ozone and subsequently rising OH radical concentrations (Figure 1A). For these reaction conditions, the RO_2 formation pathways basically governed the appearing RO_2 radical concentrations and loss processes, other than unimolecular pathways, were less important. The good agreement of results of different detection methods between themselves as well as between measured and calculated $CH_3C(O)CH_2O_2$ concentrations indicates the accuracy of the measurements. The $HO\text{-}C_9H_{12}(O_2)_xO_2$ radical with x = 1, initially formed from the OH + 1,3,5-trimethylbenzene reaction, is a bicyclic

species with an endo-peroxide group beside the peroxy radical moiety.[14a] The corresponding RO_2 radicals with x = 2 and 3 are most likely formed via repetitive intra-molecular H-shift with subsequent O_2 addition leading to one and two OOH groups in the molecule, respectively.[14b]

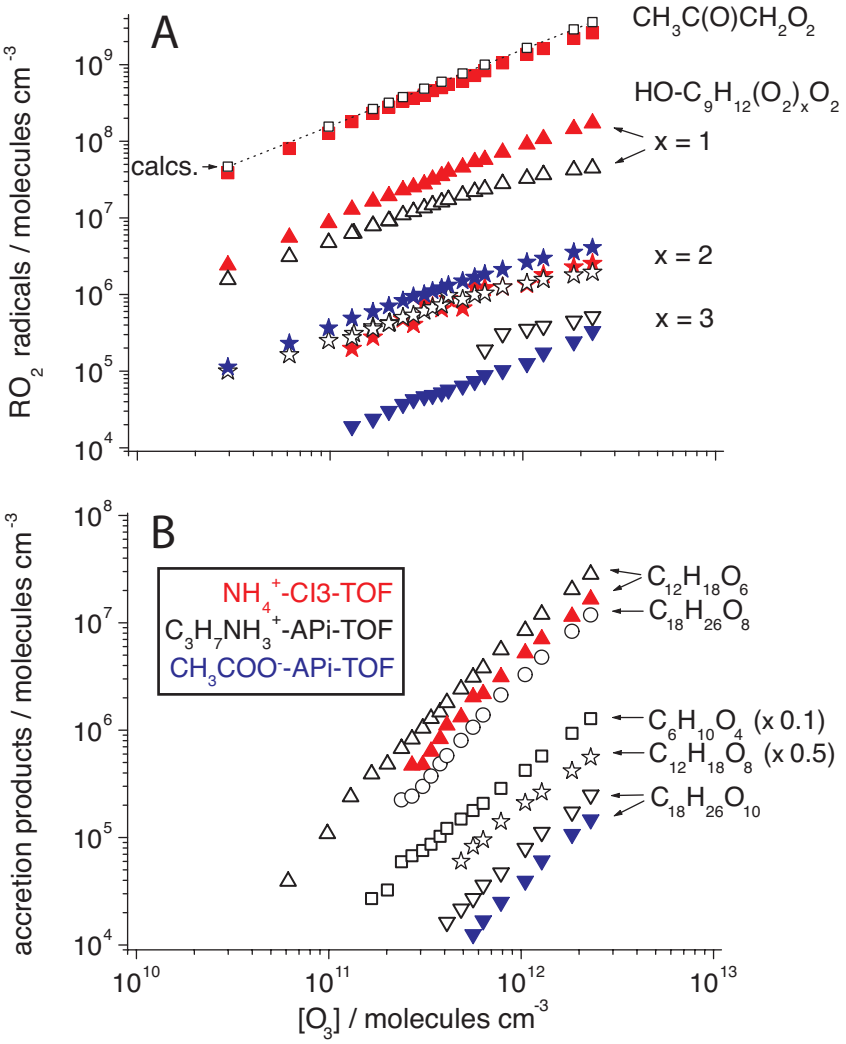
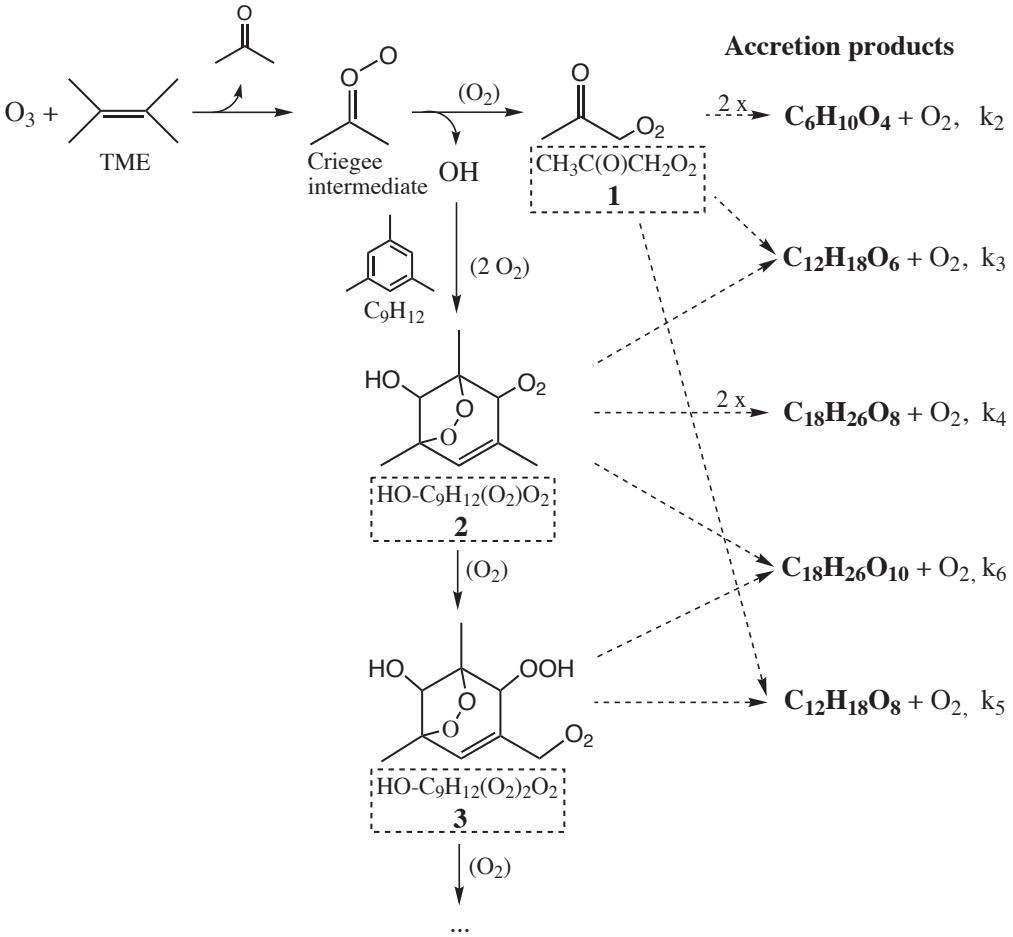


Figure 1. RO_2 radicals **A** and accretion products **B** from the reaction OH + 1,3,5-trimethylbenzene using OH radical formation via ozonolysis of TME (tetramethylethylene). Symbol coding of detection methods: red full: NH_4^+-CI3-TOF; black open: $C_3H_7NH_3^+$-APi-TOF; blue full: CH_3COO^--APi-TOF. Reactant concentrations: [TME] = 2.0×10^{11} and [1,3,5-trimethylbenzene] = 4.06×10^{12} molecules cm^{-3}. Reaction time was 7.9 s.

Besides the RO_2 radicals, also the signals of the accretion products according to pathway (1c) from self- and cross-reactions of the RO_2 radicals in the system were detected. Strongest signals appeared for the products $C_{12}H_{18}O_6$, $C_{18}H_{26}O_8$ and $C_6H_{10}O_4$ formed from the possible combinations of the two most abundant RO_2 radicals, i.e. from $CH_3C(O)CH_2O_2$ and $HO\text{-}C_9H_{12}(O_2)O_2$ (Figure 1B and Figure S3). Additional experiments confirmed that unwanted processes did not influence the product formation during the ionization in the mass spectrometer, see Supplementary Information. Proposed pathways leading to the main accretion products are illustrated in Scheme 1.



Scheme 1. Proposed pathways for the formation of accretion products from the reaction of OH radicals with 1,3,5-trimethylbenzene (C_9H_{12}) using OH radical formation via TME ozonolysis. The rate coefficients k_2 - k_6 stand for the respective RO_2 self- or cross-reactions. Structures of **2** and **3** are adopted from ref. 14.

The steeper increase of accretion product concentrations compared with that of RO_2 radicals is consistent with a 2nd order kinetics for products of pathway (1c) (Figure 1). The expected linear behaviour, [accretion product] vs. $[RO_2] \times [R'O_2]$, was well fulfilled (Figure 2). Thus, the rate coefficients k_2 - k_6 could be estimated based on the respective RO_2 and accretion product measurements as summarized in Table 1. The resulting uncertainty of the rate coefficients is assumed to be not higher than a factor of 2 - 3, see Supplementary Information.

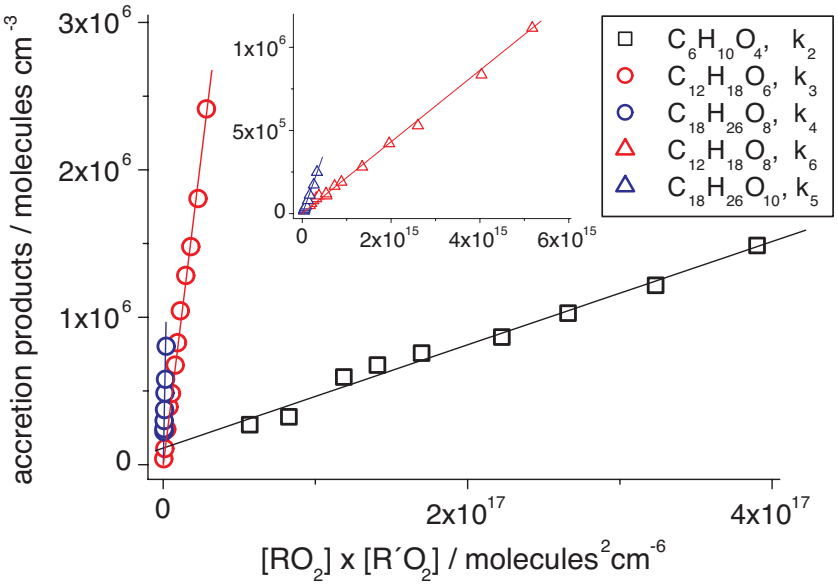


Figure 2. Kinetic analysis of accretion product formation according to pathway (1c), e.g. $RO_2 = R´O_2 =$ **1** for $C_6H_{10}O_4$, etc. Data were taken from the measurement series as depicted in Figure 1, RO_2 radicals from NH_4^+-CI3-TOF and accretion products from $C_3H_7NH_3^+$-APi-TOF measurements. For $C_6H_{10}O_4$, $C_{12}H_{18}O_6$ and $C_{18}H_{26}O_8$, only results for O_3 concentrations smaller than 5×10^{11} molecules cm^{-3} are considered.

Table 1. Rate coefficients of accretion product formation via pathway (1c) from the reaction OH + 1,3,5-trimethylbenzene using OH formation via TME ozonolysis that also forms $CH_3C(O)CH_2O_2$. The uncertainty of the k-values is assumed to be not higher than a factor of 2 - 3.

	$RO_2 + R´O_2 \rightarrow ROOR´ + O_2$ Rate coefficient (cm^3 molecule^{-1} s^{-1}) T = 295 ± 2 K		
	$R´O_2$: $CH_3C(O)CH_2O_2$ **1**	$HO\text{-}C_9H_{12}(O_2)O_2$ **2**	$HO\text{-}C_9H_{12}(O_2)_2O_2$ **3**
RO_2: $CH_3C(O)CH_2O_2$ **1**	(k_2) 1.3×10^{-12}	-	-
$HO\text{-}C_9H_{12}(O_2)O_2$ **2**	(k_3) 3.2×10^{-11} $(3.7\text{-}5.5) \times 10^{-11}$ §	(k_4) 1.4×10^{-10} $(1.7\text{-}2.5) \times 10^{-10}$ § 1.7×10^{-10} Ω	-
$HO\text{-}C_9H_{12}(O_2)_2O_2$ **3**	(k_6) 8.0×10^{-11}	(k_5) 2.6×10^{-10}	n.d.

§ from NO experiments assuming $k(NO+RO_2) = 10^{-11}$ cm^3 molecule^{-1} s^{-1}, see text
Ω from experiments using isopropyl nitrite photolysis as OH radical source
n.d.: not determined

Accretion product formation accounts for about 16% of the overall self-reaction of **1**, $k_{1c} / k_1 \sim 0.16$ ($k_1 = k_{1a} + k_{1b} + k_{1c}$), based on the obtained rate coefficient $k_{1c} = k_2$ and literature data for the overall rate coefficient k_1 [15]. An evaluation of the fraction of accretion products from other RO_2 self- and cross-reactions is impossible due to the lack of the corresponding overall rate coefficients k_1.

We tested for the influence of NO on the accretion product formation and estimated k_3 and k_4 using another independent way (Figure 3). RO_2 radical concentrations in the system decreased according to their reactions with NO. The relatively small decrease of **2** compared with that of **1** is caused by the slightly enhanced formation of OH-derived RO_2 radicals with rising NO due to additional OH radical production via $HO_2 + NO \rightarrow OH + NO_2$, see also Figure S4 for the other RO_2 radicals. The concentration of accretion products, e.g. $C_{18}H_{26}O_8$ from the self-reaction of **2** and $C_{12}H_{18}O_6$ from the cross-reaction of **1** with **2**, followed the decreasing concentrations of their RO_2 radical precursors. HO-$C_9H_{12}(O_2)ONO_2$ formation via $NO + RO_2 \rightarrow RONO_2$, RO_2 = **2**, displays the importance of the $NO + RO_2$ reaction for rising NO levels. Taking into account a $RONO_2$ yield of 0.2-0.3[16], kinetic analysis revealed that the rate coefficient k_4 of $C_{18}H_{26}O_8$ formation from the self-reaction of **2** is by a factor of 17-25 higher than that of the reaction of NO with **2** (Figure S5). Assuming $k(NO+RO_2) = 10^{-11}$ cm^3 molecule^{-1} s^{-1} [5], $k_4 = (1.7\text{-}2.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} follows in good agreement with the value determined from the NO-free measurements. Analogous analysis of $C_{12}H_{18}O_6$ formation results in $k_3 = (3.7\text{-}5.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} again in good agreement with the value from the NO-free experiments (Table 1 and Figure S6). These experiments confirm the high values of k_3 and k_4 and justify the stated uncertainty of the k-values by a factor of 2 - 3.

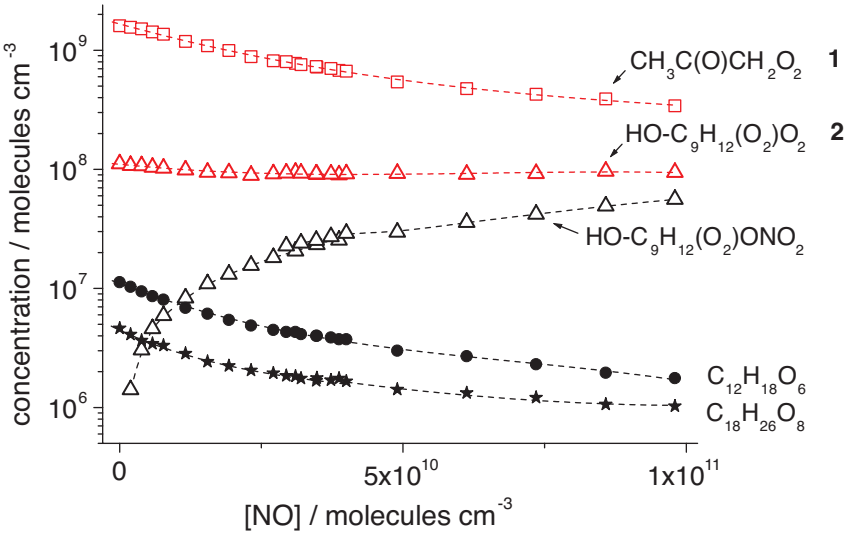


Figure 3. Main RO_2 radicals **1** and **2** and closed-shell products of **2**, i.e. the organic nitrate formed via $NO + RO_2 \rightarrow RONO_2$ and the accretion products $C_{12}H_{18}O_6$ and $C_{18}H_{26}O_8$, as a function of the NO concentration. Colour coding of detection methods: red: NH_4^+-CI3-TOF; black: $C_3H_7NH_3^+$-APi-TOF. OH radical formation via TME ozonolysis. Reactant concentrations: $[O_3] = 1.24 \times 10^{12}$, $[TME] = 2.0 \times 10^{11}$ and [1,3,5-trimethylbenzene] = 4.06×10^{12} molecules cm^{-3}.

Recent results of chamber studies point to a possible importance of ozonolysis reactions and Criegee intermediates for accretion product formation based on the identification of selected aerosol constituents.[17] In order to examine the contribution of ozonolysis products on the observed ROOR´ formation, experiments on the reaction of OH radicals with 1,3,5-trimethylbenzene were repeated in an ozonolysis-free system using isopropyl nitrite photolysis as OH radical source [18]. In the course of these experiments the RO_2 radicals HO-$C_9H_{12}(O_2)_xO_2$ with x = 1 - 3 along with the corresponding accretion products were detected well in line with the findings from the TME ozonolysis experiments (Figure S7 and Figure S8). Kinetic analysis of the $C_{18}H_{26}O_8$ formation from the self-reaction of **2** yields $k_4 = 1.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} again in very good agreement with the outcome of the other experiments (Table 1 and Figure S9). These results emphasize the accretion product formation of ROOR´ via pathway (1c) as a pure $RO_2 + R´O_2$ gas-phase reaction without any hidden effects by ozonolysis products.

Significantly higher rate coefficients than 10^{-11} cm^3 molecule^{-1} s^{-1} of accretion product formation via pathway (1c) compensate partly the higher NO concentrations that drive the competitive $NO + RO_2$

reaction in the atmosphere. Even for NO concentrations of about 10^{11} molecules cm^{-3} (4 ppbv), as it is the case in polluted urban areas, the formation of accretion products via pathway (1c) is not fully suppressed (Figure 3). Also the competitive HO_2 + RO_2 reaction, $k(HO_2+RO_2) = (0.5\text{-}2) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [5] and $[HO_2]$ in the order of 10^9 molecules cm^{-3} [2], cannot inhibit the rapid accretion product formation. Simple modelling calculations for realistic trace gas conditions in a polluted urban area confirm the importance of accretion product formation via pathway (1c), see Supplementary Information.

The general validity of product formation via pathway (1c) is demonstrated from a measurement series using 1-butene, isoprene, n-hexane or methane instead of 1,3,5-trimethylbenzene in the experiments with OH radical formation from TME ozonolysis. In each case, the corresponding accretion products from the self- and cross-reactions of OH-reaction derived RO_2 radicals, i.e. HO-$C_4H_8O_2$, HO-$C_5H_8O_2$, $C_6H_{13}O_2$ or CH_3O_2, respectively, and **1** were identified, see Supplementary Information. Resulting rate coefficients are given in Table S1. It is to be noted that also small signals appeared for CH_3OOCH_3 from the CH_3O_2 radical self-reaction in line with earlier observations.[6a] Reliable data analysis in this case, however, was impossible.

Rate coefficients of accretion product formation from the self- and cross-reactions of RO_2 radicals, as measured in this work, span a range of more than three orders of magnitude (Table 1 and Table S1). The different RO_2 reactivity in pathway (1c) is most likely connected to the RO_2 functionalization. For instance, for the self-reaction of $C_6H_{13}O_2$, **1** and **2** we obtained 9.2×10^{-14}, 1.3×10^{-12} and 1.4×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, respectively. The highest k-value is observed for **2**, HO-$C_9H_{12}(O_2)O_2$, bearing a hydroxyl and an endo-peroxide group beside the peroxy moiety[14] and the lowest for $C_6H_{13}O_2$ without an additional functional group. An analogous trend also exists for the series of reactions of **1** with other RO_2 radicals. These observations point to attractive forces from donor-acceptor relationships between functional groups of the two reacting RO_2 radicals as a necessary driving force for the rapid accretion product formation via pathway (1c).[19,20] It can be speculated at this point that based on hydrogen bonds, carbonyl or endo-peroxide groups as acceptor and hydroxyl or carboxylic groups as donor, a more stable thus longer living reactive complex is generated that finally forms the covalently bound accretion product after O_2 elimination.

Finally, the formed accretion products ROOR´ can be treated as a source for secondary organic aerosol (SOA) due to their expected low vapour pressure in the case of functionalized ROOR´. Consequently, this process of accretion product formation can help to explain missing SOA sources in the atmosphere[21], especially in urban areas characterized by high NO concentrations.[22]

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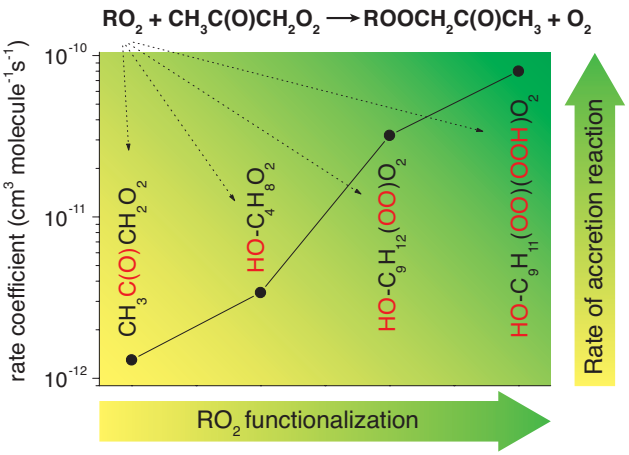

Rapid pairing up: RO_2 radicals in the atmosphere form accretion products according to $RO_2 + R´O_2 \rightarrow ROOR´ + O_2$. This pathway is very efficient in the case of functionalized RO_2 radicals reaching rates that surpass those of the competitive $NO + RO_2$ and $HO_2 + RO_2$ reactions. Accretion product formation is currently not considered in the description of atmospheric oxidation processes.

Keywords:
Atmospheric chemistry
RO_2 radical reactions
Accretion product
Mass spectrometry